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A CRITIQUE OF ATKINS' PERIODIC KINGDOM AND SOME WRITINGS ON ELECTRONIC STRUCTURE

ABSTRACT. This article consists of a critique of the writings of Peter Atkins. The topics discussed include the quantum mechanical explanation of the periodic system, the aufbau principle and the order of occupation of orbitals by electrons. It is also argued that Atkins fails to appreciate the philosophical significance of the more general version of the Pauli Exclusion Principle and that this omission has ramifications in the popular presentation of chemistry as well as chemical education and philosophy of chemistry in general.

As most chemists are aware, Peter Atkins is one of the world's most successful textbook authors and popularizers of chemistry. In this brief commentary I want to consider his book 'The Periodic Kingdom' in which the reader is taken on an imaginary geographical journey through the periodic table (Atkins, 1995). It is certainly not my intention to criticize the motivation or style of Atkins' presentation which, as in the case of his other books, is quite excellent. My aim is rather to discuss foundational issues which Atkins inevitably encounters when he turns to giving an underlying explanation for the periodic system in the later parts of this book.

Of course it might be objected that a popular book is not intended to be rigorous and that any specific criticisms that I am about to make are in fact misdirected. My response to this objection would be to remind the reader that writing in popular science, especially by somebody as expert as Atkins, should be able to interest the layperson while at the same time holding the attention and never irritating the expert. Such were the talents of Humphrey Davy and Michael Faraday, the fathers of the popular science lecture. This is the kind of balance that speakers at the Royal Institution in London are expected to try to strike, even to this day, as are authors of articles in magazines such as Scientific American and American Scientist. I

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therefore make no apologies for examining what Peter Atkins, one of the leading science popularizers, has written on the theoretical foundations of the periodic system.

I should begin by expressing my praise and admiration for the general approach that Atkins takes in his book. He starts with a description of the appearances and macroscopic properties of many of the elements with no mention whatsoever of electrons or atomic orbitals. He proceeds to discuss atomic properties, already a mistake in my view, but fortunately he takes an entirely phenomenological approach. For example, he points out that atomic radii have been measured and that, broadly speaking, they show a decrease on traversing any period and a general increase on descending any of the groups. We then begin to learn something of the history of how the periodic system gradually evolved and we are introduced to fascinating anecdotes accompanying the naming of some of the elements in the periodic system.

In part three of the book Atkins embarks on what he seems to regard as a definitive and conclusive explanation for the periodic system. He begins by developing an account of atomic orbitals, drawing on all his experience as a textbook author. At one point we are told that,

> Every p-orbital has a nodal plane of this kind, and therefore an electron which occupies a p-orbital will never be found at the nucleus. We shall see that from such minor differences spring mighty kingdoms. (Atkins, 1995, p. 111)

Atkins' approach represents an example of an all too common trend in chemistry education, that of taking the model too literally. For all we know the nodal planes may be an artifact of the model. The suggestion that nodal planes play any role whatsoever is in fact debatable. As Nelson has argued in some detail, the question of whether an electron can or cannot pass through an orbital node actually evaporates away in some interpretations of quantum mechanics (Nelson, 1990). According to some, the very question of how or whether an electron can pass through a node stems from maintaining incorrectly that an electron is a particle rather than a hybrid of a wave and a particle. In addition, according to Dirac's relativistic treatment of an electron, which has now been extended to many-electron atoms, atomic orbitals possess no nodes whatsoever. At the same time the need to incorporate relativistic effects into chemistry becomes increasingly clear even in the case of some seemingly mundane effects such as the liquid nature of mercury or the particular color of metallic gold (Fricke, 1975; Pyykkö, 1978; Norrby, 1991). The fact that the electron must be somehow able to cross a nodal plane, if one insists on talking in such terms, is taken for granted even in some general chemistry textbooks (Silberberg, 1999).

> Keep in mind that one p orbital consists of both lobes and that the electron spends equal time in both. (Silberberg, 1999, p. 283)

After enumerating the properties of atomic orbitals Atkins establishes that there are s, p, d and f type orbitals, that they come in ones, threes, fives and sevens, respectively and that each successive main shell introduces a new type of orbital as well as duplicating the type of orbitals present in the previous shell. In addition he writes,

> The total number of regions across the kingdom[1] in Period 6, which spans the disputed territory, is 32. This is twice the sum 1 + 3 + 5 + 7, the total number of orbitals. (Atkins, 1995, p. 115)

He then introduces the Pauli Exclusion Principle,

> "... that no more than two electrons can occupy any one orbital" (Atkins, 1995, p. 116)

With these two ideas in place Atkins is giving a fairly common but highly misleading alleged explanation for the periodic system. Here is a similar explanation in which the erroneous idea is spelled out in more detail, thus making it easier to examine.

> Earlier ... we saw that the total number of orbitals in each shell is equal to n^2: 1, 4, 9, or 16. Because each orbital can hold two electrons, each shell can accommodate up to $2n^2$ electrons: 2, 8, 18, or 32. We see that the beautiful structure of the periodic table reflects this orbital structure. The first row has two elements, the second and third rows have eight elements, the fourth and fifth rows have eighteen elements and the sixth row has thirty two elements ... (Brown et al., 1997, p. 211).

This kind of explanation is misleading and simply incorrect. It would only succeed if the shells were to fill sequentially, which of course they do not as soon as element 18, potassium, is reached. For example, the fourth period contains 18 elements not because the fourth shell can accommodate a total of 18 electrons but because the fourth period involves the occupation of the 4s, 3d and 3p orbitals which together happen to add to 18 electrons. There is as yet no satisfactory explanation, from first principles, to explain the atomic numbers at which the elements recur in the periodic system, namely 3, 11, 19, 37, 55, 87, to choose one group at random. What we do possess is a semi-empirical explanation that draws upon the theoretical relationship between the four quantum numbers and the experimentally obtained order of shell filling as I have recently argued (Scerri, 1998).[2]

When Atkins mentions the Pauli Principle he misses the opportunity to mention the more general version of the principle that plays a crucial role in quantum mechanics, the study of matter and more rigorous attempts to explain the periodic system. This more general version, which Atkins regularly discusses in his more advanced textbooks, states that the wavefunction for a system of fermions such as electrons is antisymmetric on the interchange of any two particles (Atkins and Friedman, 1997, p. 219)

Gone are the references to the quantum numbers of particular electrons or, in elementary terms, we lose the ability of identifying electrons in the atom and of assigning them to particular orbitals. The older version of the principle becomes strictly invalid. Quantum Mechanics, as compared with the old quantum theory, no longer permits talk of assigning four quantum numbers to a particular electron in a many-electron atom. Although Atkins regularly trots out this more general version he appears to have missed its philosophical importance when it comes to discussing atomic orbitals, the aufbau principle and the explanation for the periodic system.[3]

The point is that not only orbital assignments but also the aufbau principle becomes strictly invalid or, at best, a useful approximation but still a figment of the mathematical model. It would not be inappropriate to mention something of this situation even in a popular exposition of ideas in chemistry and the periodic system, as I will continue to press.

Atkins proceeds to take the reader carefully through the aufbau principle, one atom at a time, until he arrives at argon.

> When a subshell has its full complement of electrons (two for an s-subshell, six for a p-subshell, ten for a d-subshell and fourteen for an f-subshell), we say that that subshell is complete. When the s- and p-subshells of a given shell are both

complete we say that the shell itself is complete. The d- and f-subshells are treated slightly differently from their more dominant cousins the s- and p-subshells, in as much as, by convention, they do not need to be complete for the shell itself to be classified as complete. (Atkins, 1995, pp. 122–123)

I must say this is one of the oddest statements I have heard in many years of analyzing the explanations offered for the aufbau process. Atkins seems to imply that it is common practice to say that a shell is complete even though it is not in fact complete. This device is introduced presumably to face the inevitable question of why potassium and calcium fill their 4s orbital in preference to the 3d orbital. Indeed Atkins tells the reader.

We now have sufficient language to travel more articulately from rectangle to rectangle across the Isthmus.[4] (Atkins, 1995, p. 123)

This talk of relative energies of orbitals raises the vexed question of the relative energies of the 4s and 3d orbitals that has led to much recent discussion in the literature (Pilar, 1978; Scerri, 1989; Nelson, 1992; van Quickenborn et al., 1994; Melrose and Scerri, 1996; Bills, 1998). But the whole question of *why* the 4s orbital begins to fill rather than 3d is simply avoided when Atkins comes to the configurations of calcium and the following elements. Perhaps the reader is supposed to have remembered that "d- and f-subshells do not need to be complete for the shell itself to be classified as complete" and that this highly paradoxical sounding phenomenon comes into its own precisely at this point in the periodic system.

Interestingly the 4s/3d issue is no better explained in Atkins' advanced textbooks where he has persisted for many years in appealing to some very out-dated calculations made by R. Latter in the 1950s that seemed to indicate that the energy of the 4s orbital was indeed lower than that of 3d (Latter, 1955). However, in his recent sixth edition of 'Physical Chemistry' Atkins at least acknowledges recent research over this question by listing several of the articles I alluded to earlier, including two of my own. But unfortunately the main text shows little sign of having benefited from these new developments, since Atkins merely reproduces the commonly found graph, which is now known to be erroneous, showing the crossing-over of the energies of the 4s and 3d orbital energies. According to Hartree–Fock calculations, as Pilar has pointed out, and subsequent articles on this question have emphasized, the 4s orbital never has a lower energy than 3d, regardless of which atom is being considered (Pilar, 1978).

Atkins brings the chapter to a close by adding insult to injury when he says:

> We should note that this first long period, the first period of the Isthmus, comes into existence quite naturally. It is a sign of the strength in science that a new phenomenon does not need a new principle for its elucidation. (Atkins, 1995, pp. 123–124)

One is tempted to protest that in fact the proffered explanation does indeed require a new principle, namely the strange notion whereby the d- and f-subshells do not need to be complete for the shell itself to be classified as complete. The chapter closes triumphantly with,

> Our journey here is ended, with the kingdom rationalized and the empirical cartographers justified. (Atkins, p. 124)

Surely it would not have detracted from the triumph of science to admit at this point, or anywhere in the book, that the assignment of electrons to particular orbitals is an approximation. In fact, Atkins could have made his story of the Periodic Kingdom all the more interesting if he had stated that even though his discussion was based around an approximate concept, we are still able to use it to remarkable effect to explain so many macroscopic and microscopic features connected with trends in the periodic table.

But then on page 133 Atkins shows rather conclusively that he has not understood the philosophical implication of quantum mechanics for the orbital approximation.

> All these deep foundations of society, from the animation of organisms to the viability of industry, are at root making use of the reality of the abstract concept of the d-orbital, deep below in the engine rooms of the kingdom. (Atkins, 1995, p. 133).

What I think he should have said is that since the explanation works rather well it is tempting to regard orbitals and configurations realistically. The philosophical lesson here is that the ability of a model or theory to merely ‘Save the Phenomena’ does not entitle one to infer the truth of the model or theory but only its empirical adequacy.

Moreover, in this particular case it is not a question of philosophical taste, since quantum mechanics shows categorically that the assignment of electrons to orbitals cannot strictly be maintained in many-electron systems[5] (Scerri, 1991).

In addition, the failure to provide an adequate explanation of the 4s/3d question or a deductive explanation of the precise places where the elements appear to 'recur' should give us and Atkins grounds for suspecting that this model is not even all that empirically adequate. But Atkins, anticipating possible anti-reductionist sentiments among his readers, then says,

> It was a great achievement of the early chemists – with the crude experimental techniques available but also with the astonishing power of human reason . . . to discover this reduction of the world to its components, the chemical elements. Such reduction does not destroy its charm but adds understanding to sensation, and this understanding only deepens our delight. (Atkins, 1995, p. 147).

True enough, reduction deepens our delight when it is successful. What we really have here is a failure to explain at least two important features that are at the heart of the periodic system[6], thus suggesting the need for a deeper theory or a deeper form of reduction. To say as much would be more intellectually honest than to convey the wrong impression to the unsuspecting reader. But Atkins does not relent in his triumphant language,

> As so often in the development of science, comprehension springs from simple concepts that operate just below the surface of actuality, and constitute the true actuality. Once atoms were known – and their constitution elucidated in terms of that great invention of the mind, quantum mechanics – the foundation of the kingdom was exposed. Simple principles – the enigmatic exclusion principle, in particular – showed that the periodicity of the kingdom was a representation of the periodicity of the electronic structure of atoms. The structure, layout, and probable extensions of the kingdom are now fully understood. (Atkins, 1995, p. 148)

The situation is not fully understood. Rather we have begun to understand it. Indeed, Atkins may well be doing popular science a disservice by implying that everything is perfectly explained, and adopting precisely the kind of smug attitude that prevents many people from taking more interest in science. My own recommendation, for what it is worth, is that in chemical education and popular science writing alike one should try to "say it like it is".

NOTES

1. Atkins refers to the whole periodic table as the kingdom throughout the book.
2. I do not claim any originality for pointing this out. It has been commented on by Löwdin and it is something that computational chemists are well aware of. For example, the noted physicist Schwinger devoted considerable attention to this problem but was unable to obtain a fully satisfactory solution (Schwinger, 1980).
3. The only work that the more general version of the Pauli Exclusion Principle is made to do, even in Atkins' most advanced textbook, is to show why only even values of the J quantum number are allowed in the rotational spectrum of a molecule like CO_2.
4. Atkins calls the s and p blocks 'rectangles' while the 'Isthmus' means the d block or transition metals.
5. For a many-electron atom or molecule the commutator [H, ℓ_x] is non-zero. This implies that eigenvalues corresponding to the angular momenta operators corresponding to individual electrons are not good quantum numbers and cannot be said to characterize the motion. Instead, the vectorial sum of all the individual angular momentum operators, or L, acts as a good quantum number, but only in the absence of spin-orbit coupling. Another way of stating this result is that the individual electrons in a many-electron atom are not in stationary states but that the atom as a whole possesses stationary states. Similar arguments can be made for the other quantum numbers and these likewise imply the breakdown of the notion of four quantum numbers to characterize each electron in many-electron systems.
6. I refer to the 4s/3d question and the question of predicting from first principles the precise positions at which the elements recur (Scerri, 1998).

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